CO oxidation on gold surfaces studied on the atomic scale

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The interaction of small gold crystal tips with oxygen gas and CO/O_2 gas mixtures was studied by means of field ion microscopy (FIM). High-resolution FIM-images of clean tips were obtained with hydrogen and neon as imaging gas. At temperatures between 300 and 450 K the exposure of a clean Au sample to O_2 gas at 100–1000 mbar, in the absence of an electric field, led to oxygen chemisorption and formation of a "surface oxide". The presence of an electric field of 12–15 V/nm was found to enhance the oxidation process. Exposure to CO gas at 300 K led to the removal of the surface oxide. This was associated with the occurrence of a wave front which started in the apex centre and extended to the outskirts of the tip sample. The build-up of the surface oxide and its titration by carbon monoxide was completely reversible. Our results strongly suggest that pure gold crystals are active catalysts for the CO oxidation at 300 K.

KEY WORDS: field ion microscopy (FIM); gold; carbon monoxide; chemisorption; surface chemical reaction; oxidation

1. Introduction

For many years, gold was considered to be little reactive and, therefore, non-interesting for applications in heterogeneous catalysis. However, a number of recent studies by different research groups [1] have shown that supported gold-based catalysts can have high activity and selectivity for a variety of reactions. For example, such catalysts have proven to be highly active in the low-temperature oxidation of CO (for a recent review see [2]). On the other hand, earlier basic studies have shown that clean, low-index Au single crystal surfaces are inactive towards adsorption of O_2 gas at 300 K [3]. Assuming the reaction to proceed according to a Langmuir–Hinshelwood mechanism between CO_{ad} and O_{ad}, the absence of dissociative adsorption of oxygen leads to an apparent contradiction. In order to solve the problem, different scenarios were discussed based on spillover effects (followed by reaction on either support or Au particles) or reaction in the interface region of Au metal and promoter or support [4]. In addition, as discussed in [1,5,6], the size of the supported Au particles plays an important role in catalytic performance. In summary, however, it is fair to say that the mechanism responsible of the CO/O_2 reaction on Au-based catalysts is not clear at present.

This letter reports on the reactivity of small Au particles in the absence of any oxidic support. We resort to field ion microscopy (FIM) since the apex of a metal field emitter represents an excellent model of a single catalyst grain exposing different kinds of planes and sites. Results will be presented that prove that oxygen can be activated on stepped surfaces of an Au tip and subsequently react with CO at ambient temperature.

2. Experimental

A detailed description of the experimental setup can be found elsewhere [7]. The field ion microscope is part of an all-metal UHV system with residual gas pressures in the 10^{-10} mbar range. The system consists of several chambers and a magnetically driven rod allows samples to be transferred back and forth without exposing them to air. In one chamber, reaction studies can be performed with purified gases at pressures up to 1 bar. The analysis chamber contains a channel plate ($\varnothing = 3$ inch) image intensifier mounted on a movable rod to adjust imaging distances. Standard field ion micrographs can be taken by a high resolution CCD-camera (512 × 512 pixels, 18 bit dynamic resolution). A closed cycle He refrigeration system allows for sample cooling with lowest achievable temperatures of $\sim$50 K. Both hydrogen and neon (99.999% purity) can be (and have been) used as imaging gases.

Reaction studies were monitored by means of a moonlight video camera with a time resolution of 20 ms, and registered on videotape. Subsequently, selected sequences of the tape were digitised to produce snapshots. Oxygen and carbon monoxide gas of commercial purity (99.998 and 99.997%, respectively) were used for the reaction experiments. Due to the large difference in the partial pressure of the reactants ($p_{CO}/p_{O_2} \approx 10^{-3}$) CO was dosed *via* a position-calibrated leak valve. During the measurements ion gauges were switched off.

Gold tips were prepared by electrochemically etching a wire ($\varnothing = 0.127$ mm, 99.99% purity) in a 20% solution of KCN in distilled water. Both (111)- and (001)-oriented samples were obtained in this manner. However, the former orientation proved to be more common and more stable in the presence of high electric fields (10–30 V/nm). The sam-

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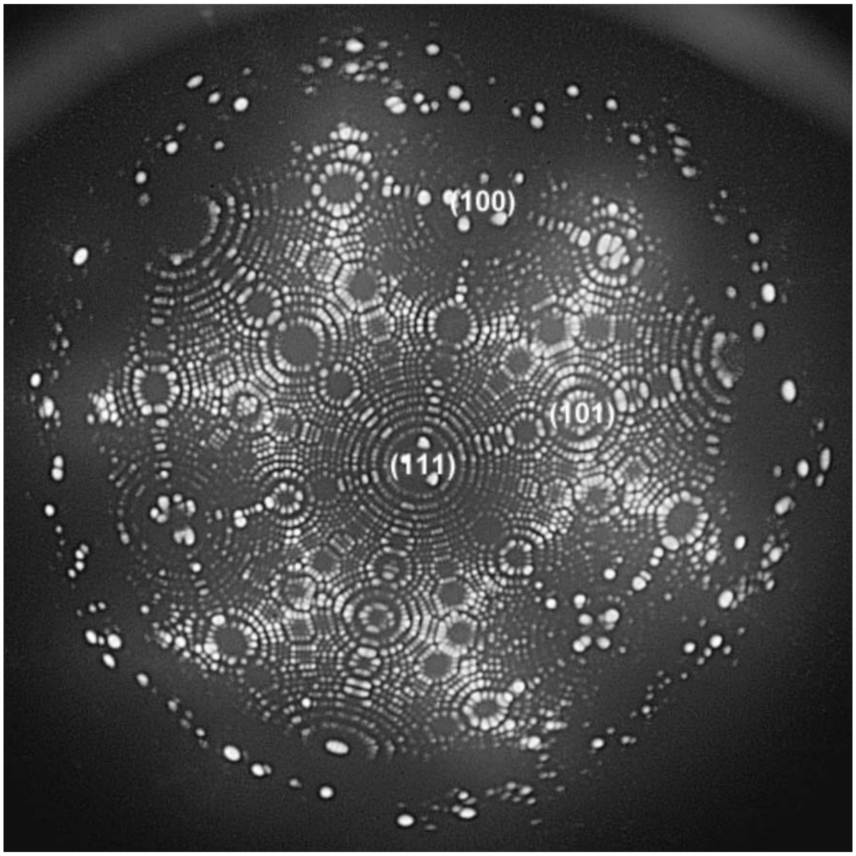

Figure 1. Field ion micrograph of a clean (111)-oriented Au sample imaged in neon at a sample temperature of 55 K. Some planes are indexed in Miller notation.

ples were usually cleaned by repeated cycles of heating in UHV and sputtering in neon.

3. Results and discussion

Figure 1 shows a field ion micrograph of a clean (111)-oriented Au tip prepared according to the procedure described above. The image was taken in neon gas at a sample temperature of 55 K and a field of 35 V/nm. Gold samples proved to be rather unstable in such high fields and, consequently, hydrogen gas was used in later stages of the preparation procedure. By counting the number of netplanes between the (111) and the {110} planes the radius of curvature of the Au sample was estimated to be 25 nm. Early FIM studies of gold metal have shown that lowering the sample temperature helps stabilising tips to increase the image quality [8]. Some planes in figure 1 are marked by their Miller indices. Due to the high contrast in the initial micrograph a filter of the software was applied which took the logarithm of each individual pixel in order to balance the color values and adjust them for printing. This procedure could not be applied to studies using video-FIM since the dynamic resolution of the video camera was not high enough.

In a first type of experiment, a clean sample was transferred to the reaction chamber and exposed to an O_2 gas atmosphere. Several experiments with pressures ranging from 100 to 1000 mbar during 20 min at temperatures between 300 and 450 K were performed. Subsequently, the gas was removed from the chamber and the specimen transferred back to the analysis chamber for imaging. Figure 2 shows an Au micrograph imaged in Ne at 55 K after exposure to $\sim$1 bar oxygen for 20 min at 450 K. Quite obviously, as compared to figure 1, changes have occurred due to the interaction with oxygen. Layer edges of (111) and {100} planes seem to be decorated by oxygen atoms. Possibly Au_xO_y clusters of a “surface oxide” have formed as indicated by arrows. It must be noted that the number of bright spots appearing in the initial stages of imaging is much higher than in figure 2. Obviously, field evaporation, *i.e.*, the ionic removal of surface atoms or compounds due to the presence of the electric field, enters in competition and prohibits imaging without destruction. Surface oxides are most fastly removed in rough surface planes due to their small size and the high local fields encountered in these regions.

In a second type of experiment we studied the interaction of oxygen and O_2/CO gas mixtures with gold surfaces under *in situ* conditions using video techniques. Accordingly, an initially clean Au specimen was exposed to an O_2 gas atmosphere of 1.0×10^{-4} mbar in the presence of an electric field of 12–15 V/nm at 300 K. While dosing, the tip was imaged with relatively uniform moderate brightness. Previous

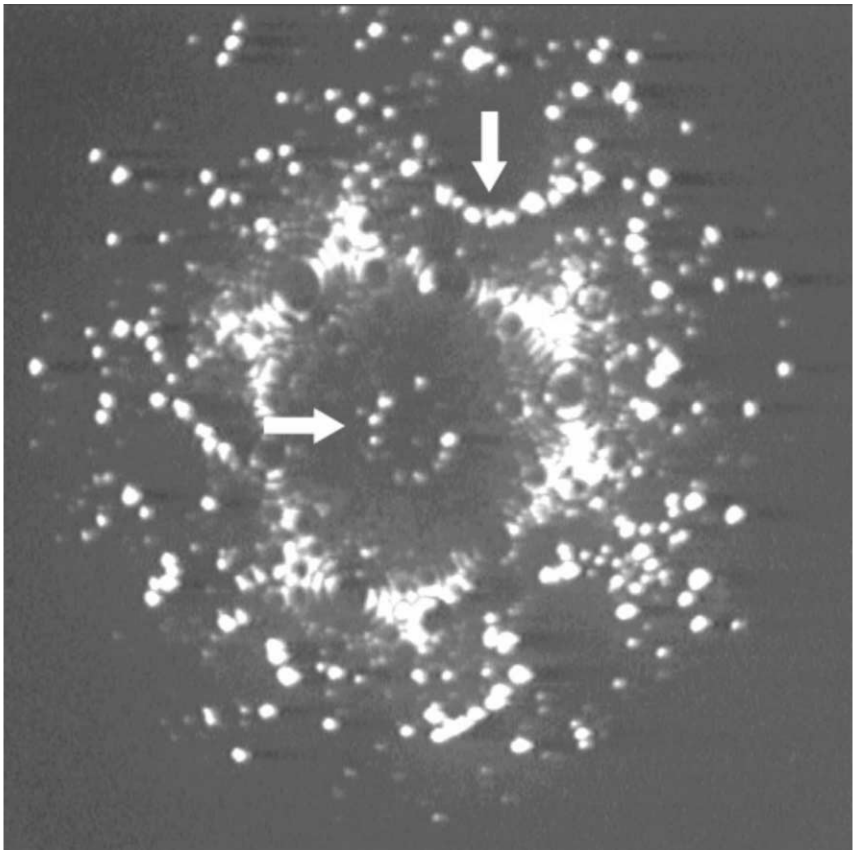

Figure 2. Same tip as in figure 1 after exposure to 1 bar O_2 gas at 450 K for 20 min. Arrows indicate the presence of a “surface oxide”.

FIM work on CO oxidation over Pt metal has demonstrated that oxygen serves as imaging gas [9]. No information about the tip symmetry could be gained from respective micrographs for which reason they are not shown here. However, in the course of the experiment bright spots appeared on the surface which increased in number and intensity with increasing time of exposure (up to 10 min). An example is shown in figure 3(a) which also serves as zero-time reference for further experiments. Interestingly, these spots vanished within a few seconds upon introduction of CO gas at 1 to 2×10^{-7} mbar. This was associated with a considerable reduction of the image brightness and led to FIM patterns similar to those observed during the early stages of imaging in pure oxygen gas (figure 3(b)).

Upon continuous exposure to the O_2/CO gas mixture (1.0×10^{-4} mbar and 2.0×10^{-7} mbar, respectively) a bright reaction front appeared in the apex centre (see arrow in figure 3(c)). On the time scale of about 60 s this front spread in nearly concentric circles towards the outskirts of the sample thereby further darkening the central part of the tip apex (figure 3 (d)–(f)). The process is reversible, *i.e.*, the video sequence leading to the series of images in figure 3 could be reproduced by closing the CO inlet valve and opening it after a time period of several minutes.

Obviously, the presence of an electric field of ∼12–15 V/nm significantly enhances the oxidation process on small gold tips. As compared to the field-free case, oxygen pressures necessary for the production of a “surface oxide layer” are several orders of magnitude lower in the presence of the imaging field. This interpretation is consistent with atom-probe measurements recently performed to analyse the chemical nature of adsorbed species in selected surface regions. Focussing the probe hole on ∼200 sites in the region of the (111) Au plane allowed us to detect AuO ionic species by field pulse desorption, in the presence of a static electric field, while exposing the gold sample to O_2 gas. A more detailed description of this work will be reported elsewhere. In a recent FIM study [10] Medvedev *et al.* found a similar behavior for the case of rhodium. In their experiments the authors also observed the appearance of a bright granular structure upon interaction of small Rh crystals with oxygen gas which was attributed to the formation of Rh_xO_y clusters. The presence of an electric field of ∼15 V/nm was found to strongly enhance the oxidation process. By adding CO it was possible to completely reduce the surface oxide which led back to the initial state of a clean tip. The behavior observed in the present experiments on gold can be interpreted in a similar manner. Accordingly, bright spots in figure 3(a) possibly represent Au_xO_y clusters. Obviously, just as in the field-free case, local enrichment of O_{ad} and cluster formation is favored over large island growth.

The bright reaction front propagating across the surface in figure 3 (c)–(f) is interpreted as being due to the removal by CO of the surface oxide. Thus, titration of O_{ad} along with CO_2 formation takes place. Areas in which O_{ad} is

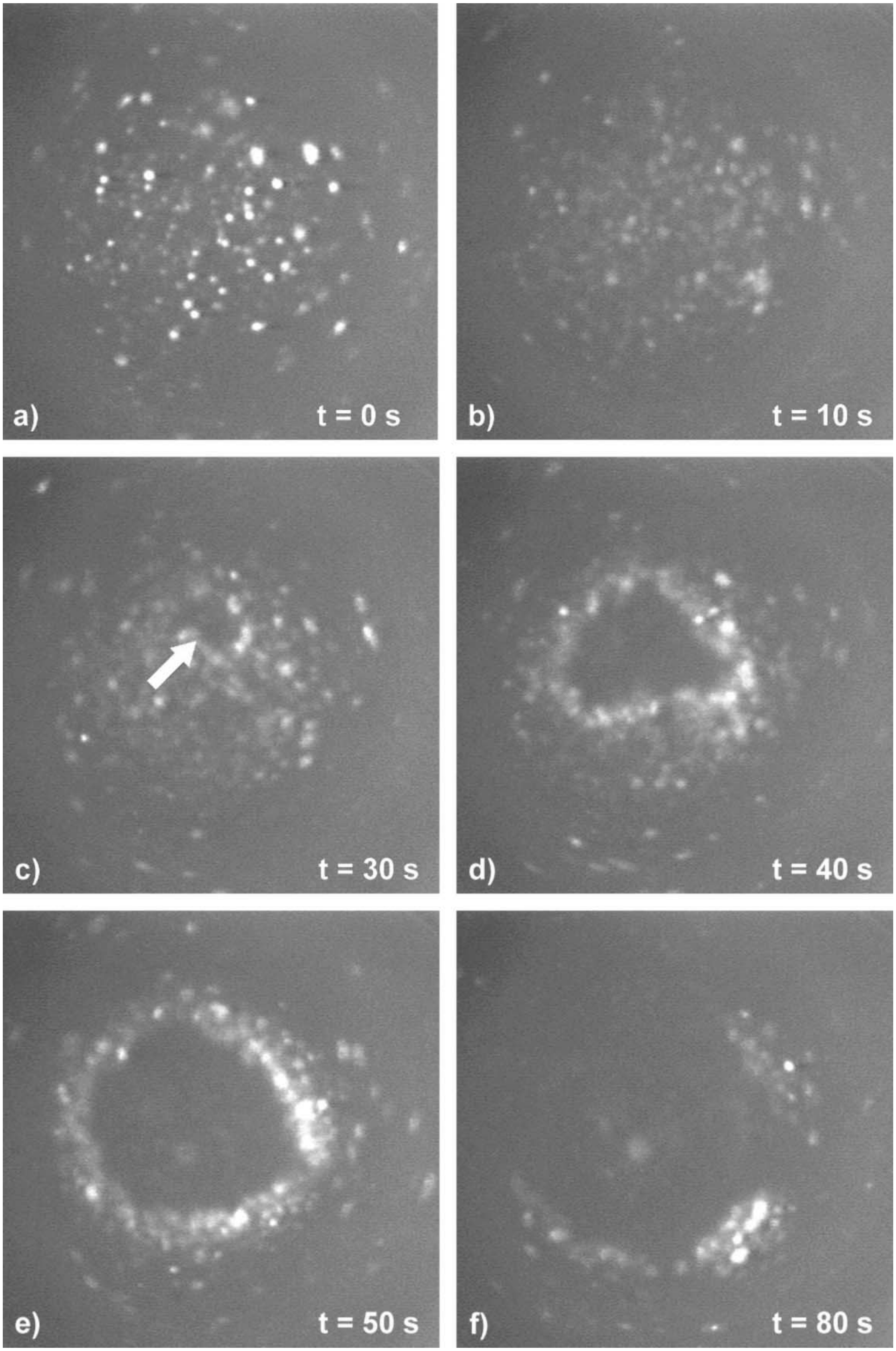

Figure 3. Sequence of images showing the reaction of surface oxygen with CO (a) and (b), and the propagation of a chemical wave due to the titration by CO (c) and (d). Experimental conditions: $T = 300$ K, $p_{O_2} = 1.0 \times 10^{-4}$ mbar and $p_{CO} \approx 2 \times 10^{-7}$ mbar (b)–(d).

replaced by CO_{ad} are imaged with much lower brightness. This is understandable in view of results obtained in adsorption experiments using field electron microscopy (FEM) at 55 K. While the image brightness decreased during O_2 adsorption on Au samples the opposite behavior was found during CO adsorption. Thus, the work function increases in the first case but decreases in the latter. Using the simple electron tunnelling model of FIM, $x_c = (I_P - \phi)/eF_{loc}$, where I_P = ionization potential, ϕ = work function, e = electronic charge and F_{loc} = local field strength, it is obvious that the critical distance for image gas ionisation is shorter in areas of high work function than in those with low work function. Consequently, the ionisation probability of O_2 molecules is higher (lower) in O_{ad} (CO_{ad}) covered regions.

Our results strongly suggest that small gold crystals with hemispherical morphology and radii of curvature of ∼20–30 nm are active catalysts for CO oxidation at 300 K. The presence of an electric field of 12–15 V/nm obviously helps activating the reactants. In particular, O_2 dissociative chemisorption is field-promoted and can be monitored *in situ* with nanoscale resolution using video-FIM. The effect of the (positive) electric field may be associated with the formation of partially charged surface metal atoms ($Au^{\delta+}$) especially in step and kink site positions. However, our results also suggest that in the absence of an electric field Au surfaces can dissociate O_2, possibly resulting in the formation of Au_xO_y clusters in edges and kinks. The clusters react with CO at room temperature.

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